Intermolecular Potentials of Mixed Systems: Testing the Lorentz-Berthelot Mixing Rules with *Ab Initio* Calculations

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ABSTRACT

The Lorentz-Berthelot mixing rules are extensively used for estimating intermolecular potential parameters between pairs of non-identical molecules (ij) from those between pairs of identical molecules (ii and jj). *Ab initio* molecular calculations allow direct estimation of intermolecular potentials in all three systems and hence afford a method of testing the Lorentz-Berthelot mixing rules.

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Executive Summary

It is necessary to model the decomposition of energetic materials (combustion for propellants and detonation for explosives) in order to gain a predictive capability for performance and safety issues of existing and potential energetic materials which may be utilised in future weapons systems.

Modelling of these decomposition processes involves sophisticated numerical models, which require equations of state describing properties of the decomposition products such as pressure, volume and internal energy. These decomposition products are largely gases, which in the high pressure, high temperature regime present during combustion or detonation, are highly non-ideal. Non-ideal behaviour of gases is largely determined by the interactions between pairs of gas molecules which can be described by intermolecular potentials. Thus we require accurate estimates of the intermolecular potentials present in gaseous products of energetic material decomposition in order to accurately model the decomposition process.

Ab Initio methods for obtaining intermolecular potentials between pairs of identical molecules (eg, H_2/H_2 or N_2/N_2) has been described previously[1]. However, in a gaseous mixture, as would be expected from a decomposition process, there will also be interactions between non-identical molecules (eg, N_2/H_2). To estimate the potential between these non-identical molecules, the Lorentz-Berthelot mixing rules are frequently used to "mix" the parameters from the systems for the two pairs of identical molecules (eg, H_2/H_2 and N_2/N_2). On the other hand, ab initio methods allow us to obtain intermolecular potential parameters directly for all three systems. This affords not only a method of accurately obtaining intermolecular potential parameters, but also of testing the Lorentz-Berthelot mixing rules.

This document compares the intermolecular potential results obtained for pairs of non-identical molecules using ab initio calculations with those obtained using the Lorentz-Berthelot rules to mix the parameters from intermolecular potentials between identical pairs of molecules. This will allow more accurate prediction of the decomposition behaviour of energetic materials, leading to a better understanding of performance and safety issues regarding weapon systems, with direct relevance to the Australian Defence Force.

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[1] White, A.; Zerilli, F.J. and Jones, H.D., *Ab Initio calculations of intermolecular potential parameters for gaseous decomposition products of energetic materials*, DSTO Technical Report, DSTO-TR-1016, August 2000.

Contents

1. Introduction

Intermolecular potentials are of use in many fields of computational chemistry, including molecular dynamics (eg [1, 2]), molecular mechanics (eg [3]) and modelling of non-ideal gases (eg [4]). The latter application is of particular interest in the study of the product gases from energetic material decomposition processes such as detonation or combustion [5, 6]. Such studies enable equations of state to be described for these gaseous products and consequently allow insights into the performance and safety of energetic materials.

Intermolecular interactions in gases are usually described by the potential between a single pair of molecules (eg, the potential between two H_2 molecules in hydrogen gas). The potential is then assumed to be additive over the whole fluid. In some cases, intermolecular potentials can be calculated from studies which examine non-ideal gas behaviour (eg [4]). Once the potential is determined, it can be fit by an equation which allows the potential curve to be reduced to a simple set of parameters.

Intermolecular potentials between pairs of identical molecules ("homomolecular pairs", eg, H_2/H_2) have been described in a previous report [5], however, in a gas mixture, interactions will also occur between pairs of non-identical molecules ("heteromolecular pairs", eg, HF/H_2). Heteromolecular intermolecular potentials are not as readily obtained as those between homomolecular pairs. One popular method for estimating intermolecular potential parameters for heteromolecular pairs is to use the Lorentz-Berthelot (LB) mixing rules (eg [7, 8, 9, 10]) to "mix" the parameters between the intermolecular potential curves for the two homomolecular systems. For example, for the mixed pair HF/H_2, the parameters for the two homomolecular systems HF/HF and H_2/H_2 would be mixed. Empirical correction factors are used to adjust the curves to fit the available information.

Ab Initio calculations allow intermolecular potential parameters to be obtained directly for both homomolecular pairs and heteromolecular pairs. Consequently, this allows an analysis of the accuracy of the Lorentz-Berthelot mixing rules.

This document compares the intermolecular potential results for some pairs of non-identical molecules obtained using *ab initio* calculations with those obtained using the Lorentz-Berthelot mixing rules. In addition, Lorentz-Berthelot correction factors are calculated and compared with literature values.

2. Methodology

2.1 Intermolecular Potentials

Intermolecular potentials are generally assumed to have some variation of the form shown in Figure 1. The potential curve arises primarily from two interactions:

(a) an attractive term at higher intermolecular distances due to so-called "van der Waals" or "dispersion" forces between instantaneous dipoles caused by electron correlation, a coupling between the motions of the electrons in each molecule. These forces are proportional to $1/r^6$ and increase rapidly with the polarizability of the molecules and the number of electrons in the molecules.

(b) a strongly repulsive term at short intermolecular distances due to nonbonded overlap between the electron clouds on each molecule and nucleus-nucleus repulsion.
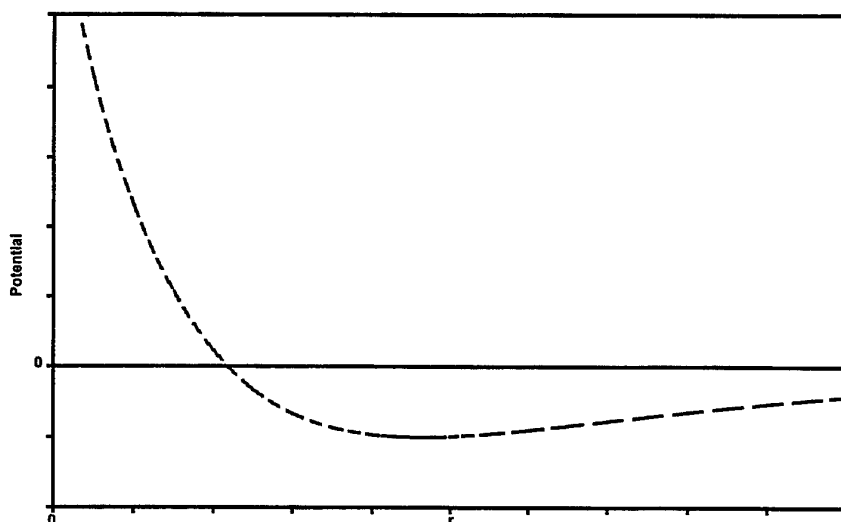
Figure 1: Variation of intermolecular potential with intermolecular distance.

Other interactions may also influence the potential curve. In particular:

(a) If the molecules are charged, strong electrostatic interactions will occur. However, in this paper, only neutral molecules are considered.

(b) If the molecules have fixed dipoles or multipoles, dipole or multipole interactions will occur, dependent on the relative molecular orientations. As discussed in Section 2.3, these effects can be averaged out to give a "spherically symmetric" potential, independent of particular relative molecular orientations.

(c) If hydrogen bonding occurs. This effect will be considered in the discussion below in cases where it arises.

One particular potential expression which is known to be particularly suitable for fitting intermolecular potential data is the exponential-6 (exp-6) potential [5]:

$$\bar{\phi} = \frac{\varepsilon_0}{(\alpha-6)}\left[6e^{\alpha\left(1-\frac{r}{r*}\right)} - \alpha\left(\frac{r*}{r}\right)^6 \right] \qquad (1)$$

The exp-6 potential curve is characterised by three parameters, as shown in Figure 2:
- ε_0 – the maximum well depth of the potential
- $r*$ – the intermolecular distance at which the maximum well depth occurs and
- α – a "steepness parameter" which describes the rate of rise of the repulsive interaction at low intermolecular distances.
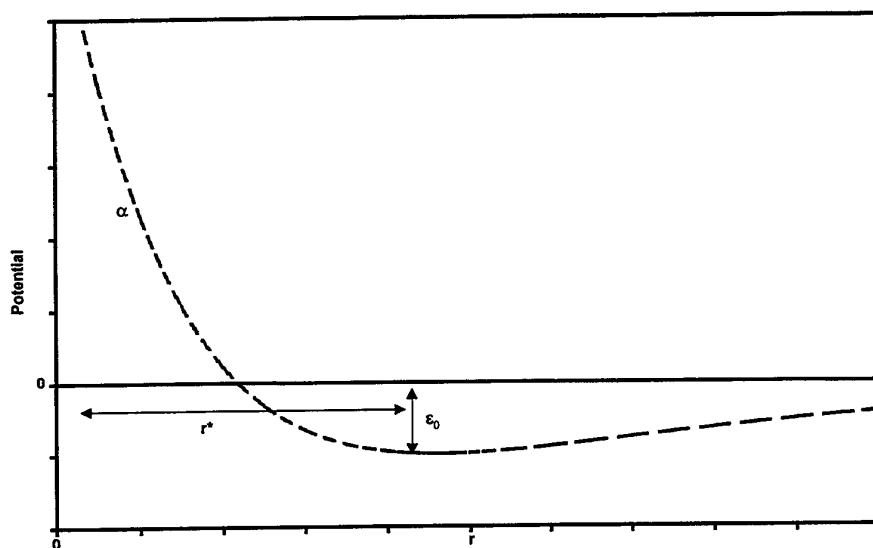

Figure 2: The exponential-6 (exp-6) potential and associated parameters.

2.2 The Lorentz-Berthelot (LB) Mixing Rules

The Lorentz-Berthelot (LB) mixing rules estimate the intermolecular potential parameters ε_0, $r*$ and α for a mixed pair of molecules (ij where i≠j) by combining the analogous potential parameters for the two pairs of identical molecules (ii and jj):

$$\varepsilon_{0ij} = k_{ij}\sqrt{\varepsilon_{0ii}\varepsilon_{0jj}}$$

$$r_{ij}^* = \frac{l_{ij}\left(r_{ii}^* + r_{jj}^*\right)}{2}$$

$$\alpha_{ij} = m_{ij}\sqrt{\alpha_{ii}\alpha_{jj}}$$

where k_{ij}, l_{ij} and m_{ij} are empirical correction factors. For example, Ree et al. [10] , in a study of the interaction of HF with other detonation products (H_2O, CO_2 and CO), set $k_{ij} = m_{ij} = 1$ and determined the values of l_{ij} using a chemical equilibrium code.

2.3 The Multipole Expansion Technique for Obtaining Spherically Symmetric Potentials

The potential field between a pair of molecules is generally asymmetric, depending on the relative orientation of the molecules. To simplify the relationships involved so that the potentials can be used in general equations of state, the asymmetric potential field can be averaged to obtain a spherically symmetric intermolecular potential, which is independent of a particular molecular orientation.

A "Multipole Expansion" (ME) method for obtaining spherically symmetric intermolecular potentials between identical pairs of axially symmetric molecules has been described previously [5]. Application of the results in obtaining equation of state information for decomposition products of energetic materials and subsequent prediction of explosive performance were described in [6].

The ME method involves, for each intermolecular distance r, obtaining the potentials of several different molecular configurations by *ab initio* calculation. These are then averaged to obtain the spherically symmetric intermolecular potential at that intermolecular distance. This procedure is repeated for various intermolecular distances in the range of interest. The exp-6 potential is used to fit the variation of intermolecular potential with intermolecular distance to derive the parameters ε_0, r^* and α described above.

All *ab initio* calculations were conducted using Gaussian 98 [11] with the Møller-Plesset fourth order method (MP4) and a 6-311++G(3df,2pd) basis set [5, 12]. The ME averages are obtained at the l=4 (hexadecapole) level as described in [5, 6]. The particular molecules discussed in the study were chosen because they are major products of energetic material decomposition and are also axially symmetric. Axially symmetric molecules have fewer orientational degrees of freedom to consider, simplifying the equations which need to be solved to obtain the spherically symmetric average. For non-axially symmetric molecules (eg, H_2O) another method can be used, such as the Monte Carlo method described in [5, 13].

3. Results and Discussion

3.1 Carbon Monoxide / Nitrogen (CO/N₂)

Four curves for systems involving CO and N_2 are shown in Figure 3:

- **CO/CO and N₂/N₂** : the ME average data points obtained directly from *ab initio* calculations on the homomolecular systems CO/CO (■) and N_2/N_2 (•) and their corresponding exp-6 curve fits. The resulting parameters are given in Table 1.

- **CO/N₂** : the ME average data points obtained directly from *ab initio* calculations on the heteromolecular system CO/N₂ (◊) and the corresponding exp-6 curve fit. The resulting parameters are also given in Table 1.

- **CO/N₂ (LB)** : the exp-6 curve for the heteromolecular CO/N₂ system derived from the parameters obtained by applying the LB mixing rules to the CO/CO and N_2/N_2 parameters. The LB parameters used to generate the curve are given in Table 1.
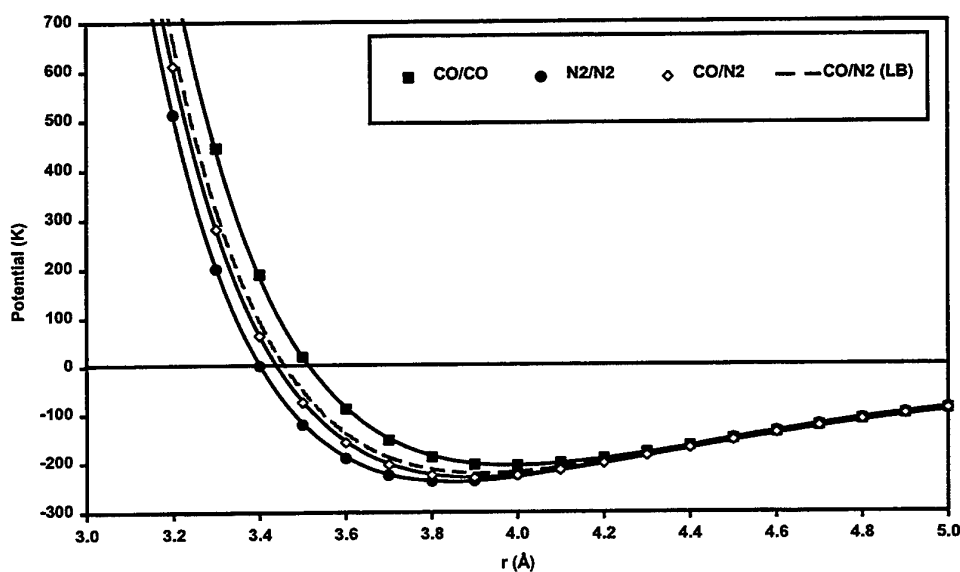
Figure 3: Average intermolecular potential curves for CO/N₂ systems.

Table 1: Intermolecular potential parameters for CO/N₂ systems

Molecular Pair	ε_0 (K)	r^* (Å)	α	Ref.
CO / CO	205.0	3.99	12.7	[1]
N₂ / N₂	238.2	3.85	13.2	[1]
CO / N₂	229.3	3.90	12.8	
CO/N₂ (LB)[1]	221.0	3.92	12.9	

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[1] Note that where LB values are quoted in this section, they are "uncorrected" in that the correction factors k_{ij}, l_{ij} and m_{ij} are all assumed to be equal to one.

As CO and N_2 are isoelectronic (have the same number of electrons), their polarizabilities and as a consequence their dispersion forces, would be expected to be very similar. This can be seen to be the case in the intermolecular potential curves (Fig. 3), where, at large intermolecular distances, the potentials are indistinguishable. However, as the intermolecular distance decreases, the average potential for CO/CO begins to rise sooner than for N_2/N_2, resulting in an apparent decrease in the maximum well-depth (ε_0) and an increase in the intermolecular distance at which the minimum is observed (r^*). Although the differences are not very large, this effect can also be seen in the parameters given in Table 1.

To explain this observed difference in behaviour between CO and N_2, the molecular orbital (MO) structures of the two molecules must be considered. Although CO and N_2 have the same *number* of electrons, their electronic structures are quite different. The valence electrons in both molecules occupy one σ and two π MOs[2] and both are conventionally drawn with triple bonds, C≡O and N≡N. However, as the CO molecule is composed of two different elements, the molecular orbital structure is distorted, because the valence atomic orbitals on oxygen ($2s$, $2p_x$, $2p_y$ and $2p_z$) are lower in energy than those on the carbon ("the oxygen is more electronegative"), causing two effects:

(a) the bonding MOs tend to be more oxygen in character ("the electrons spend more time on the oxygen") making CO slightly dipolar whereas N_2 is not. However, this effect is not expected to be significant as the ME averaging technique combines several orientations of the molecules to estimate the spherically symmetric intermolecular potential [5], counteracting the extra attraction in one orientation by the increased repulsion in another.

(b) the highest occupied molecular orbital (HOMO) in CO is an essentially non-bonding or slightly anti-bonding σ orbital, largely localised on the carbon[3] and higher in energy than the equivalent orbital in N_2, which is a bonding MO evenly distributed between the nuclei. Consequently, the C≡O bond is slightly longer than the N≡N bond (by about 0.03 Å [5]) and, when the electron clouds of two CO molecules overlap, they do so at higher intermolecular distances (increasing r^*) and are more non-bonding in character (decreasing ε_0) than in N_2.

As expected, both the curve derived using the LB mixing rules (CO/N_2(LB)) and the directly calculated CO/N_2 curve lie between those of CO/CO and N_2/N_2. This may simply be fortuitous, with the two heteromolecular curves forced to be close together

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[2] The σ and two π MOs are very close in energy. Most texts show the σ orbital higher in energy than the two degenerate π orbitals in both N_2 and CO, however, accurate ab initio calculations conducted during this work appear to indicate that in N_2 the σ orbital is lower in energy (-17.2 eV) than the π orbitals (-16.5 eV). For CO, these MOs are at -15.2 eV (σ) and -17.2 eV (π).

[3] The lowest unoccupied MOs (LUMOs) of CO are a degenerate pair of $\pi(2p)$ orbitals and this combination of a filled σ HOMO which can donate electrons to a metal ion, and an empty low-energy pair of π LUMOs accounts for the multitude of metal-carbonyl complexes observed [14].

by the similarity in the homomolecular curves, however the consistency of the results does encourage confidence in the fidelity of the *ab initio* results and the ME method.

3.2 Carbon Monoxide / Hydrogen (CO/H₂)

Given in Table 2 are the exp-6 intermolecular potential parameters for the homomolecular pairs CO/CO and H_2/H_2 obtained using the Multipole Expansion technique. For the mixed molecular pair system CO/H_2, the corresponding parameters obtained by using the LB mixing rules to combine the parameters from the homomolecular pairs are labelled CO/H_2 (LB). The results obtained directly from the *ab initio* ME calculation on the CO/H_2 mixed system are also given. The data points from which the ME parameters are derived, the curves derived from the ME parameters and the curve derived from the LB parameters are shown in Figure 4.

Table 2: Intermolecular potential parameters for CO/H₂ systems

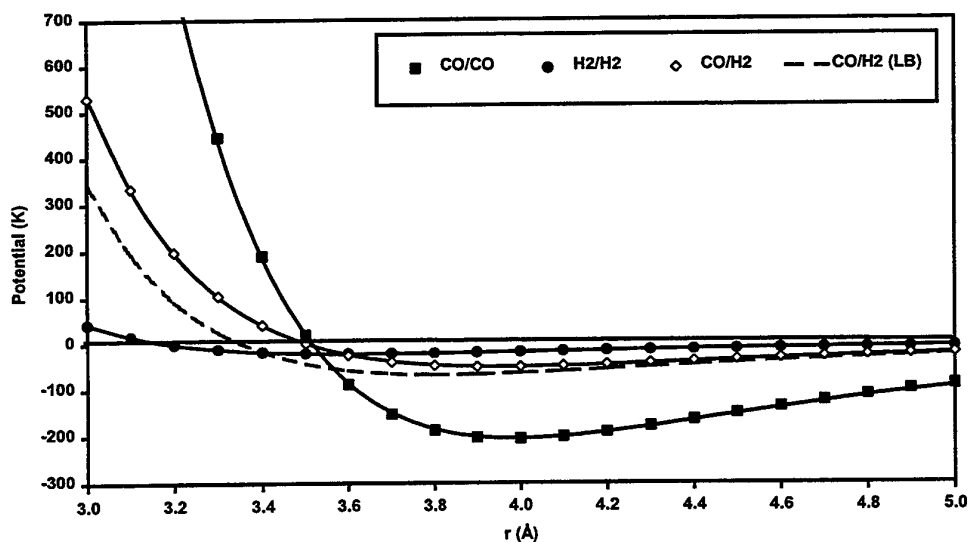| Molecular Pair	ε_0 (K)	r^* (Å)	α	Ref.
CO / CO	205.0	3.99	12.7	[1]
H_2 / H_2	22.5	3.64	12.1	[1]
CO / H_2	50.5	3.97	13.0	
CO/H_2 (LB)	67.9	3.82	12.4	

Figure 4: Average intermolecular potential curves for CO/H₂ systems.

Unlike CO and N_2 examined in Section 3, the CO and H_2 molecules are very dissimilar. The H_2 molecule has only two electrons, both involved in bonding. Consequently, it

has very low polarizability and dispersion energy between molecules, leading to a very small minimum in the potential energy (ε_0). In addition, H_2 is a very small molecule, with a bond length around 0.74 Å so that the (small) electron clouds on the molecules only begin to overlap significantly, and the repulsive interaction causing the rise in the potential curve is only apparent, at very small intermolecular distances. Consequently the potential energy minimum is also achieved at low values of the intermolecular distance (ie, r^* is low).

In contrast, the CO molecule has a bond length around 1.14 Å, it has 14 electrons and the electron cloud extends to a significant distance from the molecule. The greater number of electrons in CO increases the energy of the electron correlation effects between CO molecules, increasing the well depth (ε_0). The larger electron clouds mean that the clouds begin to interact at greater intermolecular distances, increasing r^*.

The LB results for the heteromolecular pair CO/H_2 are quite similar to those for the *ab initio* ME results (Table 2 and Figure 4). The LB curve has a slightly deeper minimum energy (ε_0) obtained at a slightly lower intermolecular distance (r^*) and a slightly lower potential rise steepness at short intermolecular distances (α)[4]. This can be explained by the disruption of the CO – CO electron correlation in going from the CO/CO system to the CO/H_2 system which is not taken into account in the uncorrected LB average.

3.3 Carbon Monoxide / Hydrogen Fluoride (CO/HF)

Given in Table 3 are the exp-6 intermolecular potential parameters from the ME method for the homomolecular pairs CO/CO and HF/HF and the heteromolecular pair CO/HF. The corresponding parameters for the latter system obtained using the Lorentz-Berthelot mixing rules to combine the parameters from the ME homomolecular pairs are labelled CO/HF (LB). The data from which the ME parameters are derived and the curve from the LB parameters are shown in Figure 5.

The maximum well-depths (ε_0) for the CO/CO and HF/HF curves happen to be very similar. In the case of CO/CO, there is a large correlation interaction between the molecules as mentioned above due to the large electron clouds present, leading to a large maximum well depth. In the case of HF/HF, the correlation interaction is lower, because hydrogen does not have a large electron cloud, however, HF does have a large permanent dipole and hydrogen bonding[5], again leading to a large energy of interaction, and again giving a large value for ε_0. On mixing these molecules in the

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[4] Of course, these differences can be corrected empirically by adjusting the Lorentz-Berthelot correction factors as will be discussed in Section 0.

[5] As explained in the CO/N_2 case, the ME method tends to average out effects due to dipole (and other multipole) moments, with one molecular configuration with a negative interaction cancelling the effect of another with a positive interaction. Consequently, hydrogen bonding is probably more important than dipole moment in this case.

CO/HF system, the correlation interaction is less than in the case of CO/CO and the hydrogen bonding is less than in the case of HF/HF. Consequently, it would be expected that overall interaction energy would be lower and the ε_0 value calculated using the *ab initio* ME method would be lower than that expected from the simple (uncorrected) LB average, which can be seen to be the case (Table 3 and Figure 5).

Table 3: Intermolecular potential parameters for CO/HF systems

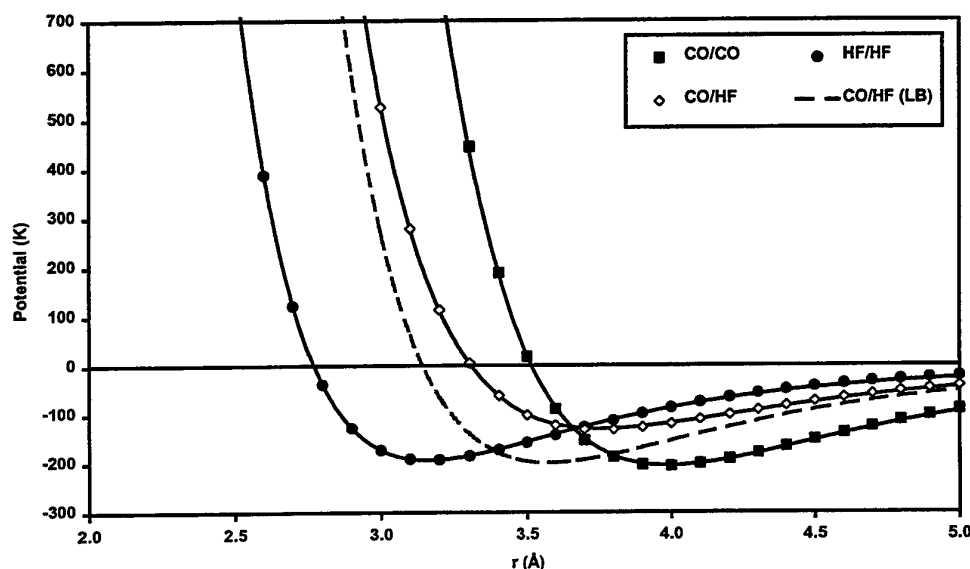| Molecular Pair	ε_0 (K)	r^* (Å)	α	Ref.
CO / CO	205.0	3.99	12.7	[1]
HF / HF	193.1	3.16	12.1	[1]
CO / HF	129.3	3.76	12.5	
CO/HF (LB)	199.0	3.58	12.4	

Figure 5: Average intermolecular potential curves for CO/HF systems.

The maximum well depth in the CO/HF system occurs at a higher intermolecular distance than would be expected from the simple LB arithmetic average of the r^* values for the CO/CO and HF/HF curves. This is probably an effect of the hydrogen bonding in HF/HF, which increases the interaction in that case and draws the molecules closer together than would be expected in the absence of hydrogen bonding. The disruption of this in the mixed case will result in a higher r^* than anticipated. Where hydrogen bonding is not an issue, such as in the CO/N_2 system in Section 3 above, it can be seen that the average r^* obtained from the Lorentz-Berthelot average is very close to that

obtained from the CO/N_2 direct calculation (Tables 1). A similar situation prevails in the CO/H_2 system (Section 3.2)[6].

3.4 Nitrogen / Hydrogen Fluoride (N_2/HF)

The parameters for the N_2/HF systems are given in Table 4 and the corresponding graphs are shown in Figure 6. It might be expected from the isoelectronic relationship between N_2 and CO that the N_2/HF system would behave in a similar manner to the CO/HF system described above (Section 3.3). In fact, the whole of the discussion given for the CO/HF system can be analogously applied to the N_2/HF system.

The maximum well-depths for the N_2/N_2 and HF/HF curves are very similar for similar reasons as those discussed above for the CO/CO and HF/HF systems. Again, on mixing these molecules in the N_2/HF system, the maximum depth of the potential curve is reduced and the minimum occurs at a higher intermolecular distance than would be expected from a simple arithmetic average of the r^* values for the homomolecular systems.

Table 4: Intermolecular potential parameters for N_2/HF systems

Molecular Pair	ε_0 (K)	r^* (Å)	α	Ref.
N_2/N_2	238.2	3.85	13.2	[1]
HF/HF	193.1	3.16	12.1	[1]
N_2/HF	159.2	3.63	12.9	
N_2/HF (LB)	214.5	3.51	12.6	

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[6] Hydrogen bonding is not present in this system, even though hydrogen is present, because the hydrogen atoms in this system are not bonded to an electronegative atom as is the case in HF.
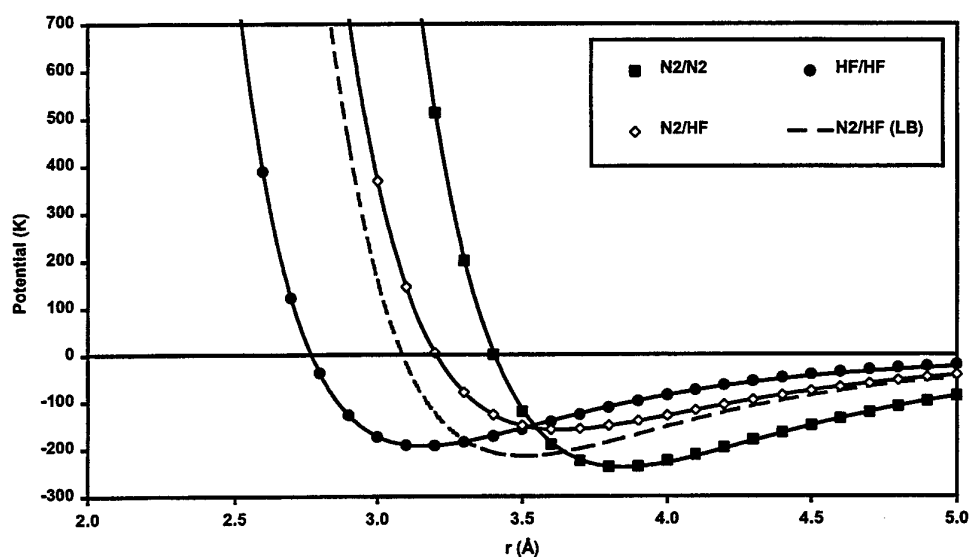
Figure 6: Average intermolecular potential curves for N₂/HF systems.

3.5 Hydrogen Fluoride / Hydrogen (HF/H₂)

The HF/H₂ system parameters are given in Table 5 and the corresponding curves are plotted in Figure 7. As discussed above in Section 3.3, there is hydrogen bonding in the HF/HF system leading to a large potential well depth (ε_0) and a small intermolecular distance at which the maximum well depth occurs (r^*). The H₂/H₂ system was discussed in Section 3.2.

Table 5: Intermolecular potential parameters for HF/H₂ systems

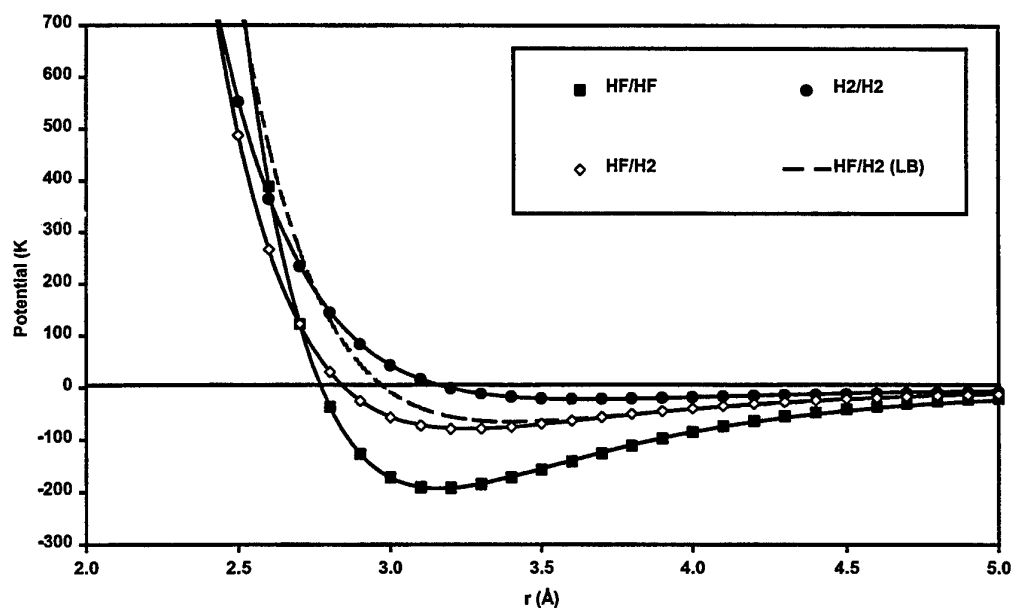| Molecular Pair	ε_0 (K)	r^* (Å)	α	Ref.
HF / HF	193.1	3.16	12.1	[1]
H₂ / H₂	22.5	3.64	12.1	[1]
HF / H₂	79.0	3.26	11.9	
HF/H₂ (LB)	65.9	3.40	12.1	

Figure 7: Average intermolecular potential curves for HF/H₂ systems.

For the mixed system, the major differences between the directly calculated HF/H₂ data and the Lorentz-Berthelot average data (HF/H₂ (LB)) is that there is found to be a greater attraction between the HF and H₂ molecules (larger well depth, ε_0 which occurs at a lower r*) than predicted. This is in contrast to the CO/H₂ case above, where the opposite was found to be true. For that system, the reason for the lower well depth and greater r* than expected could be simply explained as a disruption of the CO/CO correlation forces in the mixed system which is not allowed for in the LB average.

However, this explanation cannot be used in the HF/H₂ case, where a greater well depth and lower r* than expected are observed. It can be seen in Figure 7 that at an intermolecular distance of around 2.5 Å, the internuclear repulsion is actually less in the case of the HF/H₂ mixed system than in either the HF/HF or H₂/H₂ systems. Thus it appears that the greater well depth comes not from an increase in the attractive part of the curve, but a decrease in the repulsive part of the curve. Thus the H₂ molecule can approach an HF molecule closer than another H₂ molecule (and an HF molecule can approach an H₂ molecule closer than another HF molecule) before the rapid rise in electron cloud – electron cloud and nucleus – nucleus repulsion. Again, intuitively this makes sense. H₂ is a small molecule with only two electrons, both involved in bonding and consequently with the electron density primarily concentrated between the nuclei, which are relatively exposed. Thus there would be expected to be a strong electrostatic

repulsion (primarily nucleus - nucleus) between one H_2 molecule and another H_2 molecule approaching it. The fluorine atom in HF is much larger than the hydrogen, and is much more electronegative, carrying most of the electronic charge. Again, two approaching HF molecules would be expected to experience a strong electrostatic repulsion (negative - negative). Consequently in the HF/H_2 mixed system, there would be expected to be a greater attraction between the molecules than in either of the homomolecular systems, as is seen to be the case.

3.6 Nitrogen / Hydrogen (N_2/H_2)

The final group of systems considered here are those involving nitrogen and hydrogen. Table 6 shows the parameters for these systems and Figure 8 shows the graphs of the corresponding curves. Again, as CO and N_2 are isoelectronic, it can be seen that the N_2/H_2 set of systems is entirely analogous to the CO/H_2 set discussed in Section 3.2.

These systems are relatively simple, with homonuclear diatomic molecules, and consequently involving no dipole moments and no hydrogen bonding. Therefore one would expect that the parameters derived from the Lorentz-Berthelot mixing rules would be a reasonable approximation. This is also found to be the case, with the curve for N_2/H_2 lying very close to that for N_2/H_2 (LB).

Table 6: Intermolecular potential parameters for N_2/H_2 systems

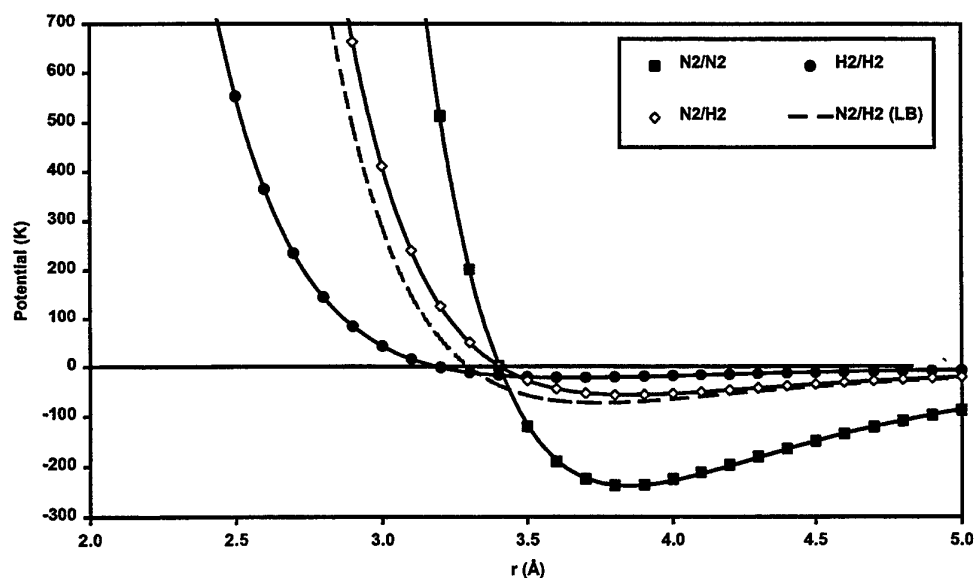| Molecular Pair	ε_0 (K)	r^* (Å)	α	Ref.
N_2 / N_2	238.2	3.85	13.2	[1]
H_2 / H_2	22.5	3.64	12.1	[1]
N_2 / H_2	57.5	3.85	13.2	
N_2/H_2 (LB)	73.2	3.75	12.6	

Figure 8: Average intermolecular potential curves for N₂/H₂ systems.

4. Comparison of Lorentz-Berthelot Results with Literature Values

The intermolecular potential parameters for each of the homomolecular systems involved in the calculations above are summarised in Table 7 labelled ME. Also in Table 7 are given the values used by Jones and Zerilli [8, 9] for CO/CO, N₂/N₂ and H₂/H₂ (labelled JZ). The JZ values are obtained by matching high-pressure data to calculations using a liquid-state perturbation theory. For the HF/HF system (labelled ZJ), the values given were obtained by Zerilli and Jones [15] from the molecular beam spectroscopic data of Barton and Howard [16]. In Table 8 the parameters for the heteromolecular systems obtained using the Lorentz-Berthelot mixing rules are summarised, along with values derived from the JZ and ZJ homomolecular parameters.

In general, the well depth predicted by the ME method is greater than the JZ or ZJ values, except for H₂/H₂. This is also reflected in the Lorentz-Berthelot figures for the mixed systems. r* and α are generally lower than the JZ or ZJ figures except again in the H₂/H₂ and HF/H₂ cases. It is not possible at this stage to definitely state which of the sets of data are more accurate.

Table 7: *Intermolecular potential parameters for homomolecular systems*

Molecular Pair	Method	ε_0 (K)	r^* (Å)	α	Ref.
CO / CO	ME	205.0	3.99	12.7	[1]
	JZ	100.0	4.12	13.3	[8, 9]
N_2 / N_2	ME	238.2	3.85	13.2	[1]
	JZ	100.0	4.12	13.3	[8, 9]
H_2 / H_2	ME	22.5	3.64	12.1	[1]
	JZ	36.0	3.46	11.1	[8, 9]
HF / HF	ME	193.1	3.16	12.1	[1]
	ZJ[7]	152.0	3.28	13.7	[15, 16]

Table 8: *Intermolecular potential parameters for heteromolecular systems derived using the Lorentz-Berthelot mixing rules*

Molecular Pair	Method	ε_0 (K)	r^* (Å)	α
CO/N_2	LB	221.0	3.92	12.9
	JZ	100.0	4.12	13.3
CO/H_2	LB	67.9	3.82	12.4
	JZ	60.0	3.79	12.2
CO/HF	LB	199.0	3.58	12.4
	JZ/ZJ	123.3	3.70	13.5
N_2/HF	LB	214.5	3.51	12.6
	JZ/ZJ	123.3	3.70	13.5
HF/H_2	LB	65.9	3.40	12.1
	ZJ/JZ	74.0	3.37	12.3
N_2/H_2	LB	73.2	3.75	12.6
	JZ	60.0	3.79	12.2

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[7] ZJ = exp-6 parameters for HF/HF at infinite temperature derived by Zerilli and Jones [9] from experimental data of Barton and Howard [10].

5. Derived Lorentz-Berthelot Correction Factors

As described in Section 1, the Lorentz-Berthelot mixing rules for obtaining intermolecular parameters ε_0, r^* and α for a mixed pair of molecules (ij, where i≠j) from those for the unmixed pairs ii and jj are:

$$\varepsilon_{0ij} = k_{ij}\sqrt{\varepsilon_{0ii}\varepsilon_{0jj}}$$

$$r_{ij}^* = \frac{l_{ij}\left(r_{ii}^* + r_{jj}^*\right)}{2}$$

$$\alpha_{ij} = m_{ij}\sqrt{\alpha_{ii}\alpha_{jj}}$$

For the sake of simplicity in the discussion above, in applying the Lorentz-Berthelot mixing rules, it was assumed that the empirical correction factors $k_{ij} = l_{ij} = m_{ij} = 1.0$, ie, for the LB curves:

$$\varepsilon_{0ij} = \sqrt{\varepsilon_{0ii}\varepsilon_{0jj}}$$

$$r_{ij}^* = \frac{\left(r_{ii}^* + r_{jj}^*\right)}{2}$$

$$\alpha_{ij} = \sqrt{\alpha_{ii}\alpha_{jj}}$$

The ability to directly measure intermolecular potentials of mixed using *ab initio* methods systems allows a direct method of obtaining ε_{0ij}, r^*_{ij} and α_{ij}. Thus, we can directly obtain values for the correction factors:

$$k_{ij} = \frac{\varepsilon_{0ij}}{\varepsilon_{0ij(LB)}}$$

$$l_{ij} = \frac{r_{ij}^*}{r_{ij(LB)}^*}$$

$$m_{ij} = \frac{\alpha_{ij}}{\alpha_{ij(LB)}}$$

For example, for the HF/H_2 system (Table 5), by dividing the value for ε_0 obtained from the *ab initio* calculation (HF/H_2) by the value obtained from the uncorrected Lorentz-Berthelot average (LB) we can obtain a value for the correction factor $k_{HF/H2}$. The other correction factors $l_{HF/H2}$ and $m_{HF/H2}$ may be analogously obtained. Derived values for the correction factors obtained for each system discussed above are given in Table 9.

The discussion of the correction factors which follows necessarily parallels that in Section 3, comparing heteromolecular curves obtained from *ab initio* calculations and those obtained from the Lorentz-Berthelot mixing rules.

Table 9: Derived Lorentz-Berthelot correction factors for heteromolecular pairs

Molecular Pair (i/j)	k_{ij}	l_{ij}	m_{ij}
CO / H_2	0.74	1.04	1.05
CO / N_2	1.04	0.99	0.99
CO / HF	0.65	1.05	1.01
HF / H_2	1.20	0.96	0.98
HF / N_2	0.74	1.04	1.02
N_2 / H_2	0.79	1.03	1.05

All the values of l_{ij} and m_{ij} are close to 1.0, probably mainly because the values of r^* and α from which they are derived are relatively small and restricted in range. For the CO/N_2 system, $k_{CO,N2}$ is close to 1.0, probably due to the isoelectronic nature of the molecules involved. However, in most cases, k_{ij} differs markedly from 1.0. $k_{CO,H2}$, $k_{CO,HF}$, $k_{HF,N2}$ and $k_{N2,H2}$ are all significantly less than 1.0 whereas $k_{HF,H2}$ is significantly greater than 1.0. A value of k_{ij} less than 1.0 ($\varepsilon_{ME(ij)} < \varepsilon_{ME(LB)}$) implies that the intermolecular attraction is lower than would be anticipated from a simple geometric average of ε_{ii} and ε_{jj}. This is found to be the case in most instances (Table 9), probably as a result of disruption of intermolecular forces on mixing which appear to be stronger in the homomolecular systems than in the mixed system. The only case where k_{ij} is greater than 1.0, implying an increase in intermolecular interaction on mixing is $k_{HF,H2}$ for reasons discussed in Section 3.5.

It should also be noted that, although the effect is small, that in Table 9 values of k_{ij} less than one are associated with values of l_{ij} and m_{ij} of greater than one. This correlation is to be expected, because if the attractive interaction is lower than expected ($k_{ij} < 1.0$), the radius of maximum interaction would be expected to be greater than expected ($l_{ij} > 1.0$) and repulsive effects will be greater than expected ($m_{ij} > 1.0$). On the other hand, a value of k_{ij} greater than 1.0 ($\varepsilon_{ME(ij)} > \varepsilon_{ME(LB)}$) implies that the intermolecular attraction is greater than anticipated ($k_{ij} > 1.0$), the radius of maximum interaction will be lower than expected ($l_{ij} < 1.0$) and repulsive effects will be lower than expected ($m_{ij} < 1.0$).

Ree et al. [10] , in a study of the interaction of HF with other detonation products (H_2O, CO_2 and CO), set $k_{ij} = m_{ij} = 1$ and determined the values of l_{ij} using a chemical equilibrium code. The value they obtained for $l_{CO,HF}$ using this method was 1.08, in close agreement with the figure of 1.05 in Table 9. The assumed value of 1.0 for $m_{CO,HF}$ appears to be reasonable, however $k_{CO,HF} = 1.0$ does not appear to be a reasonable assumption as the value obtained from the ME method (CO/HF) was 0.65. Thus if this method is to be used, it would appear to be preferable to set $l_{ij} = m_{ij} = 1.0$ and determine the value of k_{ij}.

6. Conclusions

It has been shown that *ab initio* methods are very useful in calculating intermolecular potentials in both homomolecular and heteromolecular (mixed) systems. It appears that the Lorentz-Berthelot (LB) mixing rules should be used with caution in estimating intermolecular potentials in heteromolecular systems.

The assumption that the Lorentz-Berthelot correction factors l_{ij} and m_{ij} are equal to 1 appears to be reasonable, at least for the cases tested here, however, the correction factor k_{ij} is not usually equal to 1 and this should not be assumed. In one case, CO/N_2, where the species are isoelectronic, k_{ij} was found to be very close to 1.0. However, in most cases, k_{ij} is less than one, implying that the intermolecular interaction in the mixed system is actually lower than predicted by the LB mixing rules. This can be intuitively rationalised, because, in general, mixing two different molecules will disrupt any dispersion-dispersion or hydrogen bonding attraction in the homomolecular systems. In one case (HF/H_2), k_{ij} was found to be greater than 1.0. This situation appears to be an unusual consequence of the particular intermolecular interaction between these two molecules.

Further work is required to test the generality of the conclusions proposed here. The study of further combinations of molecules (possibly including use of the Monte Carlo method [5] to examine the effect of non-axially symmetric molecules such as H_2O [13]) would enable intermolecular relationships between pairs of non-identical molecules to be explored in much greater detail. The effect of these calculations on the accuracy of equations of state and the subsequent prediction of energetic materials performance and safety issues also needs to be investigated.

7. Acknowledgments

8. References

1. Rapaport, D.C., The art of molecular dynamics simulation, Cambridge University Press, Cambridge (1995).

2. Haile, J.M., Molecular dynamics simulation: elementary methods, John Wiley and Sons, New York (1992).

3. Schlecht, M.F., Molecular modelling on the PC, John Wiley and Sons, New York (1998).

4. Atkins, P.W., Physical chemistry, W.H. Freeman and Co, San Francisco (1978).

5. White, A.; Zerilli, F.J. and Jones, H.D., Ab Initio calculations of intermolecular potential parameters for gaseous decomposition products of energetic materials, DSTO Technical Report (in publication).

6. White, A.; Zerilli, F.J. and Jones, H.D., An ab initio method for estimating equation of state parameters, American Physical Society Conference on Shock Compression of Condensed Matter, Snowbird, Ut (1999).

7. Allen, M.P. and Tildesley, D.J., Computer Simulation of Liquids, Clarendon Press, Oxford (1989).

8. Jones, H.D. and Zerilli, F.J., Theoretical equation of state for aluminized nitromethane, J. Appl. Phys., 69, 3893-3990 (1991).

9. Jones, H.D. and Zerilli, F.J., Multipole effects on the equation of state for reaction products of explosives, 10th International Detonation Symposium, 449 (1995).

10. Ree, F.H.; Viecelli, J.A. and van Thiel, M., Equation of state of insensitive high explosives, 11th Detonation Symposium, Snowmass, Co (1998).

11. Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Scuseria, G.E.; Robb, M.A.; Cheeseman, J.R.; Zakrzewski, V.G.; Montgomery, J.A. Jr.; Stratmann, R.E.; Burant, J.C.; Dapprich, S.; Millam, J.M.; Daniels, A.D.; Kudin, K.N.; Strain, M.C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G.A.; Ayala, P.Y.; Cui, Q.; Morokuma, K.; Malick, D.K.; Rabuck, A.D.; Raghavachari, K.; Foresman, J.B.; Cioslowski, J.; Ortiz, J.V.; Stefanov, B.B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R.L.; Fox, D.J.; Keith, T.; Al-Laham, M.A.; Peng, C.Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P.M.W.; Johnson, B.; Chen, W.; Wong, M.W.; Andres, J.L.; Gonzalez, C.; Head-Gordon,

M.; Replogle, E.S. and Pople, J.A. (1998) *Gaussian 98, Rev. A.3*, Gaussian Inc., Pittsburgh PA.

12.   Dorsett, H. and White, A., Overview of molecular modelling and *ab initio* molecular orbital methods suitable for use with energetic materials, DSTO General Document (in publication).

13.   White, A. *Ab Initio* calculation of intermolecular potential parameters for H_2O, DSTO Technical Note (in preparation).

14.   Cotton, F.A.; Wilkinson, G.; Murillo, C.A. and Bochmann, M., Advanced Inorganic Chemistry, 6th ed., John Wiley and Sons, New York (1999).

15.   Zerilli, F.J. and Jones, H.D., High pressure equation of state for HF, CF_4 and F_2, in High Pressure Science and Technology-1993, AIP Conference Proceedings 309, American Institute of Physics, New York, 113 (1994).

16.   Barton, A.E. and Howard, B.J., An intermolecular potential-energy surface for $(HF)_2$, Faraday Discuss. Chem. Soc., 73, 45-62 (1982).

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19. ABSTRACT
The Lorentz-Berthelot mixing rules are extensively used for estimating intermolecular potential parameters between pairs of non-identical molecules (ij) from those between pairs of identical molecules (ii and jj). *Ab Initio* molecular calculations allow direct estimation of intermolecular potentials in all three systems and hence afford a method of testing the Lorentz-Berthelot mixing rules.